



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US96/17224 <b>(22) International Filing Date:</b> 25 October 1996 (25.10.96)  <b>(30) Priority Data:</b> 60/008,893      19 December 1995 (19.12.95)      US  <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).  <b>(72) Inventors:</b> SCHIFFINO, Rinaldo, S.; 4215 Meadow Forest Lane, Kingwood, TX 77345 (US). CROWTHER, Donna, J.; 1104 Cactus Drive, Baytown, TX 77521 (US).  <b>(74) Agents:</b> MULLER, William, G. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims and statement.</i>
<b>(54) Title:</b> HIGH TEMPERATURE SOLUTION POLYMERIZATION PROCESS  <b>(57) Abstract</b> <p>This invention is a solution process for the preparation of high molecular weight ethylene-<math>\alpha</math>-olefin-diolefin copolymers comprising contacting ethylene, one or more <math>\alpha</math>-olefin monomers, and optionally one or more diene monomers, with a catalyst system at a polymerization temperature at or above about 80 °C, ethylene, one or more <math>\alpha</math>-olefin monomers, and optionally one or more diene monomers, with a catalyst system comprising an unbridged Group 4 metal compound having a bulky monocyclopentadienyl ligand, a uninegative bulky Group 15 ligand and two uninegative, activation reactive ligands and a catalyst activator compound. The process can be advantageously practiced at a reaction temperature of at least 80 °C, most preferably above 100 °C, to achieve high number average molecular weight polymer having high <math>\alpha</math>-olefin monomer and diene monomer contents with high diene conversion rates. The process is particularly suitable for the preparation of elastomeric ethylene-propylene or ethylene-propylene-diene monomer elastomers.</p>		

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## HIGH TEMPERATURE SOLUTION POLYMERIZATION PROCESS

### Technical Field

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This invention relates to the preparation of high molecular weight ethylene-containing copolymers under high temperature solution coordination polymerization conditions using catalyst systems based on monocyclopentadienyl derivatives of Group 4 metals.

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### Background of the Invention

Polymers comprising ethylene and at least one or more  $\alpha$ -olefin and optionally one or more diolefin make up a large segment of polyolefin  
15 polymers and will be addressed for convenience as "ethylene- $\alpha$ -olefin-diolefin copolymers" herein. Such polymers range from crystalline polyethylene copolymers to largely amorphous elastomers, with a new area of semi-crystalline "plastomers" in between. In particular, ethylene- $\alpha$ -olefin-diolefin elastomers are a well established class of industrial polymers having a  
20 variety of uses associated with their elastomeric properties, their thermo-oxidative stability, their solubility in hydrocarbon oleaginous fluids, and their capability for modifying the properties of polyolefin blends. Included in this terminology are the commercially available EPM (ethylene-propylene monomer) and EPDM (ethylene-propylene-diene monomer) rubbery polymers,  
25 both being vulcanizable by cross-linking, the addition of the diolefin, also known as diene monomer, providing increased ease of both cross-linking and functionalization.

Commercially prepared ethylene- $\alpha$ -olefin-diolefin elastomers have been  
30 traditionally been made via Ziegler-Natta polymerization with homogenous catalyst systems largely based on vanadium or titanium. Newer metallocene catalyst compounds have received attention due to their ease of larger monomer incorporation and potential increases in polymerization activities. Although broadly described as suitable for polyolefin solution polymerization  
35 processes, metallocene catalysts have shown limitations in their molecular weight capabilities. Due to relatively fast termination (or chain transfer) reactions, such as the  $\beta$ -hydride elimination reaction, metallocene catalysts

tend to produce polymers and copolymers of low molecular weights at high temperatures ( $M_n$  not more than about 50,000). This problem becomes more pronounced when the  $\alpha$ -olefin comonomer content is relatively high (above 10 mol.%), which further depresses the molecular weight. In addition, the incorporation of diolefins at high conversions are important, for example in the efficient production of effectively curable EPDM rubbers.

Japanese unexamined patent application publication 94-80683 describes unbridged monocyclopentadienyl Group 4-6 metal compounds said to provide benefits for polypropylene polymerization and exemplifies the production of atactic polypropylene with (cyclopentadienyl) (bistrimethylsilylamide) titanium dichloride activated with methylalumoxane at 40 °C. The catalyst is said to be an active catalyst for polyolefin polymerization at temperatures of from -100 °C to 200 °C, desirably at -50 °C to 100 °C. Synthesis of this catalyst is described here and in "Dialkylamido derivative of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_3]$ ,  $[(\eta^5\text{-C}_5\text{Me}_5\text{TiCl}_2)_2(\mu\text{-O})]$  and  $[(\eta^5\text{-C}_5\text{Me}_5\text{TiCl})_3(\mu\text{-O})]$ : X-ray crystal structure of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ti}(\text{NMe}_2)_3]$ ", Mart'n *et al.*, *Journal of Organometallic Chemistry*, 467 (1994), 79-84.

Catalyst systems based on monocyclopentadienyl titanium compounds activated with alumoxane suitable for the preparation of ethylene- $\alpha$ -olefin copolymers of high molecular weight and high  $\alpha$ -olefin content are described in U.S. patent 5,264,405. This patent teaches that the cyclopentadienyl group should be fully substituted with methyl groups and bridged to an amido group having an aliphatic or alicyclic hydrocarbyl ligand bonded through a 1° or 2° carbon. Copolymerization of ethylene with propylene in Example 45 with a bridged monocyclopentadienyl Group 4 metal catalyst compound at 80 °C produced a copolymer with 20 wt.% ethylene having an  $M_n$  of about 20,080. In each Example 55 with the same catalyst as with Example 45, at a reaction temperature of 140 °C, an ethylene-propylene copolymer having a density of 0.863, indicative of an amorphous ethylene copolymer, exhibited an  $M_n$  of about 46,500.

U.S. patent 5,321,106 describes a broad class of Group 4 or Lanthanide series metal compounds useful as addition polymerization catalysts for ethylenically unsaturated monomers where activated by a cationic oxidizer, the compounds comprising an anionic or non-anionic ligand system ("L"), one

of several being -NR<sub>2</sub> where R is a hydrocarbyl, silyl, germyl, or a substituted hydrocarbyl, silyl, germyl group of from 1 to 24 carbon, silicon, or germanium atoms. The preferred catalysts are monocyclopentadienyl compounds having a divalent substituted cyclopentadienyl group linked through a Y heteroatom  
5 ligand, inclusive of nitrogen heteroatoms, to the Group 4 or Lanthanide series metal. Polymerization example 2 illustrates a preferred catalyst used for copolymerization of ethylene and 1-octene at a temperature of 150 °C

The most commercially interesting molecular weight for elastomeric  
10 ethylene- $\alpha$ -olefin-diolefin copolymers exceeds about 50,000 M<sub>n</sub>. Further, the incorporation of high levels of diolefins, beyond those commercially provided by traditional Ziegler catalysts, is highly desired for improved capabilities for cross-linking in vulcanizates and in graft functionalization with non-hydrocarbyl moieties for improved compatibility and applications requiring  
15 greater affinity to non-hydrocarbyl chemical compounds. Additionally, the use of high temperature solution processes provide the potential for industrial benefits in ease of handling the amorphous elastomers since their solubility in the polymerization solvent increases and solution viscosity is accordingly decreased. A traditional bottleneck in the manufacture of  
20 elastomeric polymers at high temperatures is their resulting low molecular weight. Thus an ability to capitalize on inherent solution viscosity improvements at operating temperatures higher than about 80 °C while retaining high molecular weight polymers with high comonomer content is important.

25

#### Invention Disclosure

The invention is a solution process for the preparation of high molecular weight ethylene- $\alpha$ -olefin-diolefin copolymers comprising contacting  
30 ethylene, one or more  $\alpha$ -olefin monomer, and optionally one or more diene monomer, with a catalyst system prepared from at least one a catalyst activator and at least one unbridged Group 4 metal compound having a bulky monocyclopentadienyl ligand, a uninegative bulky amido ligand and two uninegative, activation reactive ligands at a polymerization temperature  
35 between about 80 °C and 160 °C. By use of the invention process copolymer having high number average molecular weight (M<sub>n</sub>), high  $\alpha$ -olefin incorporation and high diolefin conversion to incorporated monomer can be

prepared under economically advantageous reaction temperatures. In particular, ethylene- $\alpha$ -olefin-diolefin elastomers and plastomers of molecular weights greater than 55,000  $M_n$  can be prepared under the high temperature reaction conditions.

5

### Best Mode and Examples of the Invention

The ethylene- $\alpha$ -olefin-diolefin copolymer elastomer or plastomer, of this invention (hereinafter referred to as "EPC") is meant to include  
10 copolymers, terpolymers, tetrapolymers, etc. It typically comprises ethylene, one or more alpha-olefins, and optionally, one or more diene monomers; it is typically substantially amorphous; and it will typically have a substantially random arrangement of at least the ethylene and the alpha-olefin monomers. Though focused on EPC, the process will have utility for polyethylene  
15 copolymers (having ethylene and one or more  $\alpha$ -olefin comonomer such as described herein) having lower incorporation of the comonomers such that it is not elastomeric or plastomeric as defined below but useful otherwise in the manner known in the art for such crystalline and semi-crystalline polymers. Typically the polyethylene copolymers will have a polymer density of 0.86 to  
20 0.93, while the elastomers generally will include those copolymers with even lower densities.

The EPC capable of preparation in accordance with the invention process generally can have a molecular weight range typically between about  
25 55,000 and up to about 500,000 or higher, more typically between about 60,000 and 300,000 where the molecular weight is number-average (" $M_n$ ").

Typically elastomeric EPC is "substantially amorphous", and when that term is used to define the EPC elastomers of this invention it is to be  
30 taken to mean having a degree of crystallinity less than about 25% as measured by means known in the art, preferably less than about 15%, and more preferably less than about 10%. The three major known methods of determining crystallinity are based on specific volume, x-ray diffraction, and infrared spectroscopy. Another well-established method, based on  
35 measurement of heat content as a function of temperature through the fusion range, is carried out using differential scanning calorimetric measurements. It is known that these independent techniques lead to reasonably good

experimental agreement. The degree of randomness of the arrangement of monomers in the EPC elastomeric polymers also affects the crystallinity and is appropriately characterized by the degree of crystallinity.

5        Additionally, it is known in the art that the tendency of a particular combination of catalyst system and monomers to produce blocky, random, or alternating polymers can be characterized by the product of the reactivity ratios defined for the given monomers under the specific reaction conditions encountered. If this product is equal to 1.0, the sequence distribution will be  
10   perfectly random; the more the product is less than 1.0, the more the monomers will tend to have a "blocky" sequence distribution. Generally speaking, the segments of a polymer which crystallize are linear segments of a polymer which have a number of identical (both by chemical make-up and stereo-specific orientation) units in a row. Such segments are said to be  
15   "blocky". If there is little or no such sequential order within the segments making up a polymer chain, that chain will be very unlikely to conform itself into the correct shape to fit into the spatial order of a crystal and will accordingly exhibit a low degree of crystallinity. See, "Ethylene-Propylene Copolymers. Reactivity Ratios, Evaluation and Significance", C. Cozewith and G. Ver Strate, *Macromolecules*, Vol. 4, No. 4, 482-489 (1971). The EPC  
20   elastomers of this invention accordingly can be characterized in one embodiment by the limitation that its method for preparation has a reactivity ratio product less than 2.0, preferably less than about 1.5, and more preferably less than about 1.25.

25

The EPC of the invention will contain about 10 to about 90 weight percent ethylene, preferably about 20 to 85 weight percent ethylene. The EPC elastomers of the invention preferably contain from 35 to 75 weight percent ethylene.

30

The  $\alpha$ -olefins suitable for use in the preparation of the EPC, or for the polyethylene copolymers, are preferably  $C_3$  to  $C_{20}$   $\alpha$ -olefins, but will include higher carbon number olefins such as polymerizable macromers having up to one hundred carbon atoms, or more. Illustrative non-limiting examples of  
35   such  $\alpha$ -olefins are one or more of propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and 1-decene. Included in the term  $\alpha$ -olefins for the purposes of describing effectively copolymerized monomers are the constrained-ring cyclic

olefins such as cyclobutene, cyclopentene, norbornene, alkyl-substituted norbornenes, alkenyl-substituted norbornenes, and the higher carbon number cyclic olefins known in the art. The  $\alpha$ -olefin content of the EPC ranges depending upon selection of the specific  $\alpha$ -olefin or  $\alpha$ -olefins, being  
5 more for lower carbon number monomers, for example, about 10 to about 90 wt.%, preferably about 30 to about 80 wt.% for propylene; and, 5 to 35 mol.%, preferably 7.5 to 25 mol.% and most preferably 10 to 20 mol.% for 1-octene. The EPC plastomers typically have comonomer incorporation of from about 10 mol.% to about 25 mol.% , and the EPC elastomers typically have above  
10 about 25 mol.%  $\alpha$ -olefin incorporation. For the more crystalline polyethylene copolymers the range of comonomer incorporation will typically be below 10 mol.% and more typically below about 8 mol.% .

The diene monomers, or diolefins, useful in this invention include  
15 those typically used in known EPDM polymers. The typically used diene monomers are generally selected from the easily polymerizable non-conjugated dienes and can be straight chain, hydrocarbon diolefins or cycloalkenyl-substituted alkenes, having about 6 to about 15 carbon atoms, for example:

20

- A. straight chain acyclic dienes such as 1,4-hexadiene and 1,6 octadiene.
- 25 B. branched chain acyclic dienes such as 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 3,7-dimethyl-1,7-octadiene and the mixed isomers of dihydro-myricene and dihydro-ocinene;
- 30 C. single ring alicyclic dienes such as 1,3-cyclopentadiene; 1,4-cyclohexadiene; 1,5-cyclo-octadiene and 1,5-cyclododecadiene;
- 35 D. multi-ring alicyclic fused and bridged ring dienes such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene; bicyclo-(2,2,1)-hepta-2,5-diene; alkenyl, alkylindene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene (MNB), 5-ethylidene-2-



norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene; and

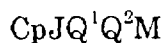
- 5 E. cycloalkenyl-substituted alkenes, such as allyl cyclohexene, vinyl cyclooctene, allyl cyclohexene, vinyl cyclooctene, allyl cyclodecene, vinyl cyclododecene.

Of these, the preferred dienes are dicyclopentadiene, 1,4-hexadiene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene and 5-vinyl-2-norbornene. Particularly preferred dienes are 5-ethylidene-2-norbornene and 1,4-hexadiene. It will be apparent that a mix of such dienes can also be utilized. The content of the optional diene monomer in the EPC elastomer can be 0 to about 20 weight percent, and if used, preferably 0.5 to about 15 weight percent, and most preferably about 2.0 to about 12.0 weight percent. Surprisingly, diene incorporation greater than 5.0 wt.%, even greater than either 8.0 wt.% or 10.0 wt.% is made possible using the process of this invention. The content of the optional diene monomer in the plastomer or ethylene copolymer of the invention can range similarly as that for the EPC elastomer, but will be preferably in the lower ranges, for example 0.1 to 8 mol.%.

The unbridged Group 4 metal compounds of this invention typically comprise Group 4 transition metals having ancillary ligands including a substituted, bulky cyclopentadienyl ligand, a substituted, bulky Group 15 heteroatom ligand, the cyclopentadienyl ligand and heteroatom ligands not covalently bound, and two uninegative, activation reactive ligands at least one of which that can be abstracted for activation of the remaining metal compound to a catalytically active state and one of which is either similarly abstractable or has a sigma bond to the transition metal into which an olefin or diolefin can insert for coordination polymerization.

Thus the unbridged monocyclopentadienyl metallocene compounds of the present invention can be represented by the formula:

35



wherein:

M is Zr, Hf or Ti;

5 Cp is a bulky cyclopentadienyl ring which is substituted with  
from two to five substituent groups R, and each  
substituent group R is, independently, a radical selected  
from hydrocarbyl, silyl or germyl radicals having from 1 to  
20 carbon, silicon or germanium atoms, substituted  
10 hydrocarbyl, silyl or germyl radicals as defined wherein  
one or more hydrogen atoms is replaced by a halogen  
radical, an amido radical, a phosphido radical, an alkoxy  
radical, an aryloxy radical or any other radical containing  
a Lewis acidic or basic functionality; C<sub>1</sub> to C<sub>20</sub>  
15 hydrocarbyl-substituted metalloid radicals wherein the  
metalloid is selected from the Group IV A of the Periodic  
Table of Elements; halogen radicals; amido radicals;  
phosphido radicals; alkoxy radicals; or alkylborido  
radicals; or, Cp is a cyclopentadienyl ring in which at  
20 least two adjacent R-groups are joined together and along  
with the carbon atoms to which they are attached form a  
C<sub>4</sub> to C<sub>20</sub> ring system which may be saturated, partially  
unsaturated or aromatic, and substituted or  
unsubstituted the substitution being of one or more R  
25 group as defined above;

J is the substituted, bulky Group 15 heteroatom ligand which is  
substituted with two substituent groups R<sup>1</sup>, and each  
substituent group R<sup>1</sup> is, independently, a radical selected  
30 from hydrocarbyl, silyl or germyl radicals having 1 to 20  
carbon, silicon or germanium atoms, substituted  
hydrocarbyl, silyl or germyl radicals as defined wherein  
one or more hydrogen atoms is replaced by a halogen  
radical, an amido radical, a phosphido radical, an alkoxy  
radical, or an aryloxy radical; C<sub>3</sub> to C<sub>20</sub> hydrocarbyl-  
35 substituted metalloid radicals wherein the metalloid is  
selected from the Group IV A of the Periodic Table of

Elements; halogen radicals; amido radicals; phosphido radicals; alkoxy radicals; or alkylborido radicals; and,

5 each Q is independently a radical selected from halide; hydride; substituted or unsubstituted C<sub>1</sub> to C<sub>20</sub> hydrocarbyl; alkoxide; aryloxide; amide; halide or phosphide; or both Q together may be an alkylidene or a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand, with the proviso that where any Q is a hydrocarbyl  
10 radical, such Q is not a substituted or unsubstituted cyclopentadienyl radical.

Such compounds can also include an L<sub>w</sub> complexed thereto wherein L is a neutral Lewis base such as diethylether, tetrahydrofuran,  
15 dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and "w" is a number from 0 to 3.

The term "cyclopentadienyl" refers to a 5-member ring having delocalized bonding within the ring and typically being bound to M through  
20 η<sup>5</sup>-bonds, carbon typically making up the majority of the 5-member positions.

Examples of the unbridged monocyclopentadienyl metallocene compounds of the invention include:  
pentamethylcyclopentadienyltitaniumbistrimethylsilylamido dichloride,  
25 tetramethylcyclopentadienyltitaniumbistrimethylsilyl-amidodichloride, pentaphenylcyclopentadienyltitanium bistrimethylsilylamidodichloride, pentabenzylcyclopentadienyl titaniumbistrimethylsilylamidodichloride, tetraphenyl- cyclopentadienyltitaniumbistrimethylsilylamidodichloride, tetraphenylcyclopentadienyltitaniumbistrimethylsilylamido dichloride,  
30 bistrimethylsilylcyclopentadienyltitanium bistrimethylsilylamidodichloride, trisrimethylsilylcyclopentadienyl titaniumbistrimethylsilylamidodichloride, trimethylsilyl,t-butylcyclopentadienyltitaniumbistrimethylsilylamidodichloride, bist-butylcyclopentadienyltitaniumbistrimethylsilylamidodichloride,  
35 indenyltitaniumbistrimethylsilylamidodichloride, 2-phenylindenyltitaniumbistrimethylsilylamidodichloride, 2,4-diphenylindenyltitaniumbistrimethylsilylamidodichloride,

- 2-methylindenyltitaniumbistrimethylsilylamidodichloride,  
2-methyl,4-phenylindenyltitaniumbistrimethylsilylamidodichloride,  
fluorenyltitaniumbistrimethylsilylamidodichloride,  
pentamethyl
- 5 cyclopentadienyltitaniumtrimethylsilyltriphenylsilylamidodichloride,  
tetramethylcyclopentadienyltitaniumtrimethylsilyltriphenylsilyl  
amidodichloride,  
pentaphenylcyclopentadienyltitaniumtrimethyl-  
silyltriphenylsilylamidodichloride,
- 10 pentabenzylcyclopentadienyl-  
titaniumtrimethylsilyltriphenylsilylamidodichloride,  
tetraphenylcyclopentadienyltitaniumtrimethylsilyltriphenylsilyl-  
amidodichloride,  
tetraphenylcyclopentadienyltitaniumtrimethylsilyl
- 15 triphenylsilylamidodichloride,  
bistrimethylsilylcyclopentadienyl-  
titaniumtrimethylsilyltriphenylsilylamidodichloride,  
tristimethylsilylcyclopentadienyltitaniumtrimethylsilyl-  
triphenylsilylamidodichloride,
- 20 trimethylsilyl,t-butylcyclopentadienyl  
titaniumtrimethylsilyltriphenylsilylamidodichloride,  
bistbutylcyclopentadienyltitaniumtrimethylsilyltriphenylsilyl-  
amidodichloride,  
indenyltitaniumtrimethylsilyltriphenylsilyl- amidodichloride,
- 25 2-phenylindenyltitaniumtrimethylsilyltriphenyl-silylamidodichloride,  
2,4-diphenylindenyltitaniumtrimethylsilyl- triphenylsilylamidodichloride,  
2-methylindenyltitanium trimethylsilyltriphenylsilylamidodichloride,  
2-methyl,4-phenyl-  
indenyltitaniumtrimethylsilyltriphenylsilylamidodichloride,
- 30 fluorenyltitaniumtrimethylsilyltriphenylsilylamidodichloride,  
pentamethylcyclopentadienyltitaniumbistriphenylsilylamido-dichloride,  
tetramethylcyclopentadienyltitaniumbistriphenylsilyl- amidodichloride,  
pentaphenylcyclopentadienyltitaniumbistriphenyl- silylamidodichloride,  
pentabenzylcyclopentadienyltitaniumbis- triphenyl silylamidodichloride,
- 35 tetraphenylcyclopentadienyltitanium- bistriphenylsilylamidodichloride,  
tetraphenylcyclopentadienyl- titaniumbistriphenylsilylamidodichloride,  
bistrimethylsilylcyclopentadienyltitaniumbistriphenylsilylamidodichloride,

- tristrimethylsilylcyclopentadienyltitaniumbistriphenylsilyl-amidodichloride,  
trimethylsilyl, t-butylcyclopentadienyl-  
titaniumbistriphenylsilylamidodichloride,  
bist-butyl cyclopentadienyltitaniumbistriphenylsilylamidodichloride,  
5 indenyltitaniumbistriphenylsilylamidodichloride,  
2-phenylindenyltitaniumbistriphenylsilylamidodichloride,  
2,4-diphenylindenyltitaniumbistriphenylsilylamidodichloride,  
2-methylindenyltitaniumbistriphenylsilylamidodichloride,  
2-methyl,4-phenylindenyltitaniumbistriphenylsilylamidodichloride,  
10 fluorenyltitaniumbistriphenylsilylamidodichloride,  
pentamethylcyclopentadienyltitaniumbistriisopropylsilyl-amidodichloride,  
tetramethylcyclopentadienyltitaniumbis- triisopropylsilylamidodichloride,  
pentaphenylcyclopentadienyl- titaniumbistriisopropylsilylamidodichloride,  
pentabenzyl- cyclopentadienyltitaniumbistriisopropylsilylamidodichloride,  
15 tetraphenylcyclopentadienyltitaniumbistriisopropylsilylamido-dichloride,  
tetraphenylcyclopentadienyltitaniumbistriisopropylsilyl- amidodichloride,  
bistrimethylsilylcyclopentadienyltitaniumbistriiso-  
propylsilylamidodichloride,  
tristrimethylsilylcyclopentadienyl-  
20 titaniumbistriisopropylsilylamidodichloride,  
trimethylsilyl,t-  
butylcyclopentadienyltitaniumbistriisopropylsilylamidodichloride,  
bist-butylcyclopentadienyltitaniumbistriisopropylsilylamido- dichloride,  
indenyltitaniumbistriisopropylsilylamidodichloride,  
25 2-phenylindenyltitaniumbistriisopropylsilylamidodichloride,  
2,4-diphenylindenyltitaniumbistriisopropylsilylamidodichloride,  
2-methylindenyltitaniumbistriisopropylsilylamidodichloride,  
2-methyl,4-phenylindenyltitaniumbistriisopropylsilyl amidodichloride,  
fluorenyltitaniumbistriisopropylsilylamidodichloride,  
30 pentamethylcyclopentadienyltitaniumtriisopropyltrimethylsilyl-  
amidodichloride,  
tetramethylcyclopentadienyltitaniumtriisopropyl-  
trimethylsilylamidodichloride,  
pentaphenylcyclopentadienyl-  
35 titaniumtriisopropyltrimethylsilylamidodichloride,  
pentabenzylcyclopentadienyltitaniumtriisopropyltrimethylsilyl  
amidodichloride,

- tetraphenylcyclopentadienyltitaniumtriisopropyl-  
trimethylsilylamidodichloride,  
tetraphenylcyclopentadienyltitanium-  
triisopropyltrimethylsilylamidodichloride,  
5 bistrimethylsilylcyclo-  
pentadienyltitaniumtriisopropyltrimethylsilylamidodichloride,  
tristrimethylsilylcyclopentadienyltitaniumtriisopropyltrimethylsilyl-  
amidodichloride,  
trimethylsilyl, t-butylcyclopentadienyl-  
10 titaniumtriisopropyltrimethylsilylamidodichloride,  
bist-butyl-cyclopentadienyltitaniumtriisopropyltrimethylsilylamidodichloride,  
indenyltitaniumtriisopropyltrimethylsilylamidodichloride,  
2-phenylindenyltitaniumtriisopropyltrimethylsilylamidodichloride,  
2,4-diphenylindenyltitaniumtriisopropyltrimethylsilyl amidodichloride,  
15 2-methylindenyltitaniumtriisopropyltrimethylsilyl- amidodichloride,  
2-methyl,4-phenylindenyltitaniumtriisopropyl-  
trimethylsilylamidodichloride,  
fluorenyltitaniumtriisopropyltrimethylsilylamidodichloride,  
pentamethylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
20 tetramethylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
pentaphenylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
pentabenzylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
tetraphenylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
tetraphenylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
25 bistrimethylsilylcyclopentadienyltitaniumbistributylsilylamido-dichloride,  
tristrimethylsilylcyclopentadienyltitaniumbistributylsilyl-amidodichloride,  
trimethylsilylt-butylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
bist-butylcyclopentadienyltitaniumbistributylsilylamidodichloride,  
indenyltitaniumbistributylsilylamidodichloride,  
30 2-phenylindenyltitaniumbistributylsilylamidodichloride,  
2,4-diphenylindenyltitaniumbistributylsilylamidodichloride,  
2-methylindenyltitaniumbistributylsilylamidodichloride,  
2-methyl,4-phenylindenyltitaniumbistributylsilylamidodichloride,  
fluorenyltitaniumbistributylsilylamidodichloride.

Substituted versions where a hydride, hydrocarbyl, germyl or silyl group replaces one or both chlorides are suitable in accordance with invention particularly where ionizing anion precursors are activators. Separate or *in situ* alkylation is typical, e.g., dimethyl replacing dichloride.

A generic characterizing feature of these invention compounds is the inclusion of the bulky substitution on both of the cyclopentadienyl and amido ligands. It is believed that the inclusion of these bulky substituents provides kinetic stability so that the active metal center is stabilized to the high temperature reaction conditions preferably employed. Thus the inclusion of five methyl groups on the Cp ring with two trimethylsilyl groups on the amido group sufficiently stabilizes an unbridged monocyclopentadienyl titanium compound such that it approaches the temperature stability of the bridged monocyclopentadienyl titanium compounds typically said to be the preferred, highly preferred and most highly preferred compounds in prior art discussions, see for example, U.S. patents 5,064,802 and 5,321, 106.

The unbridged monocyclopentadienyl metallocene compounds according to the invention may be activated for olefin polymerization catalysis in any manner sufficient both to remove or complex one Q group such that the metal center becomes sufficiently electron deficient to attract olefinically unsaturated monomers and such that the other Q bond is either itself, or is abstracted and substituted with another Q bond, sufficiently weak so as to permit insertion of it into the olefinically unsaturated monomer to yield a growing polymer, in the manner of traditional coordination/insertion polymerization. The traditional activators of metallocene polymerization art are suitable, those typically include Lewis acids such as aluminum alkyls or alumoxane compounds, and ionizing anion pre-cursors that abstract one Q so as to ionize the metal center into a cation and provide a counter-balancing noncoordinating anion.

The term "noncoordinating anion" means an anion which either does not coordinate to said transition metal cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" noncoordinating anions are those which are not degraded to neutrality when the initially formed complex

decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Noncoordinating anions useful in accordance with this invention are those which are compatible, stabilize the metallocene cation in the sense of balancing its ionic charge in a +1 state, yet retain sufficient lability to permit displacement by an ethylenically or acetylenically unsaturated monomer during polymerization. Additionally, the anions useful in this invention will be large or bulky in the sense of sufficient molecular size to largely inhibit or prevent neutralization of the metallocene cation by Lewis bases other than the polymerizable monomers that may be present in the polymerization process. Typically the anion will have a molecular size of greater than or equal to about 4 angstroms.

Descriptions of ionic catalysts for coordination polymerization comprised of metallocene cations activated by ionizing anion pre-cursors appear in the early work in EP-A-0 277 003, EP-A-0 277 004, US patents 5,198,401 and 5,278,119, and WO92/00333. These teach a preferred method of preparation wherein metallocenes (*bis* Cp and *mono* Cp) are protonated by an anionic precursors such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic and charge-balanced by the non-coordinating anion. The use of ionizing ionic compounds not containing an active proton but capable of producing the both the active metallocene cation and an noncoordinating anion is also known. See, EP-A-0 426 637, EP-A-0 573 403 and U.S. patent 5,387,568. Reactive cations other than Bronsted acids capable of ionizing the metallocene compounds include ferrocenium triphenylcarbonium and triethylsilylinium cations. Any metal or metalloid capable of forming a coordination complex which is resistant to degradation by water (or other Bronsted or Lewis Acids) may be used or contained in the anion of the second activator compound. Suitable metals include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. The description of non-coordinating anions and precursors thereto of these documents are incorporated by reference for purposes of U.S. patent practice.



An additional method of making the ionic catalysts uses ionizing anion pre-cursors which are initially neutral Lewis acids but form the cation and anion upon ionizing reaction with the metallocene compounds, for example  
5 *tris*(pentafluorophenyl) boron acts to abstract an alkyl, hydride or silyl ligand to yield a metallocene cation and stabilizing non-coordinating anion, see EP-A-0 427 697 and EP-A-0 520 732. Ionic catalysts for addition polymerization can also be prepared by oxidation of the metal centers of transition metal compounds by anionic precursors containing metallic oxidizing groups along  
10 with the anion groups, see EP-A-0 495 375. The description of non-coordinating anions and precursors thereto of these documents are similarly incorporated by reference for purposes of U.S. patent practice.

Examples of suitable anion precursors capable of ionic cationization of  
15 the metallocene compounds of the invention, and consequent stabilization with a resulting noncoordinating anion include trialkyl-substituted ammonium salts such as:

triethylammonium tetra(phenyl)boron,  
tripropylammonium tetra(phenyl)boron,  
20 tri(n-butyl)ammonium tetra(phenyl)boron,  
trimethylammonium tetra(p-tolyl)boron,  
trimethylammonium tetra(o-tolyl)boron,  
tributylammonium tetra(pentafluorophenyl)boron,  
tripropylammonium tetra (o,p-dimethylphenyl)boron,  
25 tributylammonium tetra(m,m-dimethylphenyl)boron,  
tributylammonium tetra(p-trifluoromethylphenyl)boron,  
tributylammonium tetra(pentafluorophenyl)boron,  
tri(n-butyl)ammonium tetra (o-tolyl)boron and the like;  
N,N-dialkyl anilinium salts such as:  
30 N,N-dimethylanilinium tetra(phenyl)boron,  
N,N-diethylanilinium tetra(phenyl)boron,  
N,N-diethylanilinium tetra(phenyl)n-butylboron,  
N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron and the like;  
dialkyl ammonium salts such as:  
35 di-(isopropyl)ammonium tetra(pentafluorophenyl)boron,  
dicyclohexylammonium tetra (phenyl)boron and the like;  
and triaryl phosphonium salts such as:

triphenylphosphonium tetra(phenyl)boron,  
 tri(methylphenyl)phosphonium tetra(phenyl)boron,  
 tri(dimethylphenyl)phosphonium tetra(phenyl)boron and the like.

5 Further examples of suitable anion precursors include those comprising a stable carbonium ion, and a compatible non-coordinating anion. These include:

tropillium tetrakis(pentafluorophenyl) borate,  
 triphenylmethylium tetrakis(pentafluorophenyl) borate,  
 10 benzene (diazonium) tetrakis(pentafluorophenyl) borate,  
 tropillium phenyltris-pentafluorophenyl borate,  
 triphenylmethylium phenyl-trispentafluorophenyl borate,  
 benzene (diazonium) phenyltris-pentafluorophenyl borate,  
 tropillium tetrakis (2,3,5,6-tetrafluorophenyl) borate,  
 15 triphenylmethylium tetrakis (2,3,5,6-tetrafluorophenyl) borate,  
 benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,  
 tropillium tetrakis (3,4,5-trifluorophenyl) borate,  
 benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,  
 tropillium tetrakis (3,4,5-trifluorophenyl) aluminate,  
 20 triphenylmethylium tetrakis (3,4,5-trifluorophenyl)aluminate,  
 benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) aluminate,  
 tropillium tetrakis (1,2,2-trifluoroethenyl) borate,  
 triphenylmethylium tetrakis (1,2,2-trifluoroethenyl) borate,  
 benzene (diazonium) tetrakis (1,2,2-trifluoroethenyl)borate, tropillium  
 25 tetrakis (2,3,4,5-tetrafluorophenyl)borate,  
 triphenylmethylium tetrakis (2,3,4,5-tetrafluorophenyl)borate,  
 benzene (diazonium) tetrakis (2,3,4,5-tetrafluorophenyl) borate, etc.

Where the metal ligands include Q halide moieties, such as in  
 30 (pentamethyl cyclopentadienyl) (ditrimethylsilyl amido) titanium dichloride, which are not capable of discrete ionizing abstraction under standard conditions, these moieties can be converted via known alkylation reactions with organometallic compounds such as lithium or aluminum hydrides or alkyls, alkylalumoxanes, Grignard reagents, etc. See EP-A-0 500 944, EP-  
 35 A1-0 570 982 and EP-A1-0 612 768 for processes describing the reaction of

alkyl aluminum compounds with dihalide substituted metallocene compounds prior to or with the addition of activating anion precursor compounds.

5        Known alkylalumoxanes are additionally suitable as catalyst activators, particularly for the invention metal compounds comprising the halide ligands. The alumoxane component useful as catalyst activator typically is an oligomeric aluminum compound represented by the general formula  $(R-Al-O)_n$ , which is a cyclic compound, or  $R(R-Al-O)_nAlR_2$ , which is  
10 a linear compound. In the general alumoxane formula R is a  $C_1$  to  $C_5$  alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "n" is an integer from 1 to about 50. Most preferably, R is methyl and "n" is at least 4. Alumoxanes can be prepared by various procedures known in the art. For example, an aluminum alkyl may be treated with water dissolved in an inert  
15 organic solvent, or it may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of an aluminum alkyl with a limited amount of water yields a mixture of the linear and cyclic species of the alumoxane.

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When using ionic catalysts comprising unbridged Group 4 metal cations and non-coordinating anions, the total catalyst system will generally additionally comprise one or more scavenging compounds. The term "scavenging compounds" as used in this application and its claims is meant to  
25 include those compounds effective for removing polar impurities from the reaction solvent. Such impurities can be inadvertently introduced with any of the polymerization reaction components, particularly with solvent, monomer and catalyst feed, and adversely affect catalyst activity and stability. It can result in decreasing or even elimination of catalytic activity, particularly when a metallocene cation-noncoordinating anion pair is the  
30 catalyst system. The polar impurities, or catalyst poisons include water, oxygen, metal impurities, etc. Preferably steps are taken before provision of such into the reaction vessel, for example by chemical treatment or careful separation techniques after or during the synthesis or preparation of the various components, but some minor amounts of scavenging compound will  
35 still normally be required in the polymerization process itself. Typically the scavenging compound will be an organometallic compound such as the

Group-13 organometallic compounds of 5,153,157, 5,241,025, EP-A- 638 and WO-A-91/09882 and WO-A-94/03506, noted above, and that of WO-A-93/14132. Exemplary compounds include triethyl aluminum, triethyl borane, tri-isobutyl aluminum, tri-isobutyl aluminumoxane, and tri-n-octyl aluminum, those having bulky substituents covalently bound to the metal or metalloid center being preferred to minimize adverse interaction with the active catalyst. When an alkyl aluminum or alumoxane is used as activator, any excess over the amount of metallocene present will act as scavenger compounds and additional scavenging compounds may not be necessary. The amount of scavenging agent to be used with metallocene cation-noncoordinating anion pairs is minimized during polymerization reactions to that amount effective to enhance activity. In the process described in this invention, it was found that there is an optimum contact time between the scavenger compound and the reaction mixture to maximize catalyst activity. If the contact time is too long, detrimental catalyst deactivation might occur.

The high temperature solution process for the production of the EPC elastomers or plastomers, or ethylene copolymers, in accordance with this invention improves process economics and increases product capabilities. For process economics, the combination of high reactor temperature and solvent recovery systems brings significant cost improvements. The improved economics of the high temperature solution process compared with the conventional process is related to the operation of polymerization reactor at higher polymer concentration than in conventional solution process. The higher polymer concentrations are possible due to improvement in the solution viscosity at higher temperatures. A high reactor exit temperature improves the efficiency of the solvent recovery systems resulting in improved recycling economics. High efficiency recycling systems are crucial in considering the future of solution based processes in comparison with the competitive options, such as gas phase. In addition, efficient solvent recycling also reduces the environmental impact of the process with respect to volatile organic compound emissions to meet increasingly more restrictive regulatory levels. Additionally, the use of the invention process allows for high diolefin conversion from monomer to incorporated mer unit in the polymer, thus reducing cost of separation and recycle. Typical conversion ratios of diolefin monomer can range from 20%, 30% or up to as high as 40%, and higher.

The polymerization process of the invention involves contacting the polymerizable monomers (ethylene,  $\alpha$ -olefin and, optionally diene monomer) in solution with the described ionic catalyst system, preferably at high reaction temperatures, from about 80 °C to 160 °C or above, and is suitably conducted in the following manner. The solvent is heated to reaction temperature prior to introduction into the reaction vessel. The solvent is then provided to the reaction vessel after polymerizable monomer is introduced in either liquid, gas or solution form into that reaction solvent. A reaction medium is formed comprising the solvent within which the catalyst system and monomers are contacted for the polymerization reaction. Typically, the scavenging compound is introduced into the reaction solvent to reduce or eliminate catalyst poisons present in any of the reaction medium components prior to introduction into the reactor. If the scavenging compound and activator are different, and contacted with each other for sufficient time, adverse effects on the effectiveness of that activator might occur. In this process, the activator and metallocene compound are contacted in the polymerization reaction vessel in the presence of the polymerizable monomers, comprising the *in-situ* activation.

20

Typically the reaction is conducted at pressures from atmospheric to 500 psig (1-35 bar), preferably from 100 to 300 psig (8 to 21 bar). Preferred reaction temperatures are above 80 °C, more preferably at or above 100 °C, for instance 110 °C and above. Preferably the upper limit to the reaction temperature in this solution process is not greater than 160 °C, preferably 150 °C. Typically the polymerization reaction will be exothermic and the reactor will be chilled or cooled in accordance with known methods to assure that temperatures do not exceed those reasonably suitable for the polymer being produced.

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The feedstock purification prior to introduction into the reaction solvent follows standard practices in the art, e.g. molecular sieves, alumina beds and oxygen removal catalysts are used for the purification of ethylene,  $\alpha$ -olefin, and optional diene. The solvent itself as well, e.g., hexane and toluene, are similarly treated. Purification of the dienes was observed to increase diene conversion, best results were obtained when the diene was fractionally distilled with  $\text{CaH}_2$  as the purification method.

35

The  $\alpha$ -olefin monomer(s) and diene monomer(s), if included, are introduced in an amount proportional to the levels of incorporation desired for the polymer to be produced and the effective reactive ratios for the polymerizable monomers in the presence of the specific catalyst chosen. In the preferred embodiment the combination of the  $\alpha$ -olefin monomer(s) in reaction solvent as introduced into the reactor and effective vapor pressure of the  $\alpha$ -olefin monomer(s) is maintained according to the rate of incorporation into the copolymer product. In an alternative embodiment, the partial pressure in the reactor will be provided by ethylene alone in which situation the  $\alpha$ -olefin monomer(s) are added solely with reaction solvent. The amounts and vapor pressure will vary according to catalyst selection and polymer to be produced, but can be empirically determined well within the skill in the art, particularly in view of the description provided in the following examples.

The catalyst activator, e.g., non-coordinating anion precursor, ionizing anionic precursor, or alumoxane, can be introduced along with or separately from introduction of the optional diolefin monomer(s), if used. The diolefin can be provided in an amount effective for its rate of reaction and rate of conversion. The catalyst activator can be provided in an amount that is equal to 0.2 to 10 molar equivalents of the Group 4 metallocene compound, preferably 0.25 to 5, and even more preferably 0.33 to 3.0, when a noncoordinating anion precursor. Typically the provision of the noncoordinating anion precursor activator will be in an effective solvent, typically an aromatic solvent such as toluene. When the activator is alumoxane, it can be used in an amount that is equal to 0.5 to 10,000 molar equivalents of the metallocene compound, preferably 0.75 to 5000, and even more preferably 1.0 to 500. Preferably the alumoxane will be used in an amount empirically determined to suffice for concurrent removal of impurities and activation, but only in such amounts as necessary to accomplish those functions. Monitoring of polymerization activity by known methods will permit on-line adjustment of alumoxane to assure neither excess nor deficit amounts are maintained for unwanted periods.

The scavenging compounds are provided separately afterwards or with one of the foregoing feedstreams, in an amount suitable to increase the activity of the catalyst but in an amount lower than that at which depression

of reactivity is observed. Typically an effective amount of the scavenging compound is about 0 (e.g., with an alumoxane activator) to 100 mol. ratio based upon the ratio of scavenging compound to activator, preferably the ratio is 0.3 to 30, and most preferably it is 0.5 to 10.

5

Promptly thereafter, preferably within not more than about 1 minute, more preferably within 30 seconds, the metallocene compound is contacted with the activator in the presence of the polymerizable monomers so as to limit the residence time of the scavenging compound with the activator. The metallocene is typically provided in an aliphatic or aromatic solvent, which can be any of those suitable as polymerization medium. For ease of reference the examples below refer to the metallocene in solvent as "catalyst solution". Though any order of activation will have at least some suitability, the order of addition described herein is particularly suitable for use with ionizing activators that provide the stabilized metallocene cation-noncoordinating anion pair. Since alumoxane can act as a suitable scavenger compound, its addition as activator in accordance with the described process eliminates the need to introduce a scavenger and the preference for limited time of contact between scavenger and activator is largely eliminated so long as the addition of the metallocene to activator containing solution is in the presence of polymerizable monomers. In this manner premature activation can be avoided.

Ethylene gas is then provided into the reaction vessel in an amount proportional to the level of incorporation desired and the effective reactive ratios for the polymerizable monomers in the presence of the specific catalyst chosen, as with the  $\alpha$ -olefin monomer(s). The polymerization starts upon contact of the monomers with the activated catalyst and the rates of supply of each of the components of the system are adjusted for stable operations at the level of production, molecular weight, monomer incorporation and equipment limitations. The reaction temperature may be permitted to exceed the initial temperature but will preferably be at all times greater than the lower limit of the ranges described above for the invention process.

The solvents for the polymerization reaction will comprise those known for solution polymerization, typically the aliphatic solvents represented by hexane, or the aromatic solvents, represented by toluene. Additional

examples include heptane, cyclohexane, and Isopar E (C<sub>8</sub> to C<sub>12</sub> aliphatic solvent, Exxon Chemical Co., U.S.). Preferably the solvent is aliphatic, most preferably it is hexane.

5            Though not strictly necessary for the solution polymerization process as described, the catalyst according to the invention may be supported for use in alternative gas phase, bulk, or slurry polymerization processes where the high temperature benefits of the catalysts are sought to be applied. Numerous methods of support are known in the art for copolymerization  
10 processes for olefins, particularly for catalysts activated by alumoxanes, any is suitable for the invention process in its broadest scope. See, for example, U.S. patent 5,227,440. An example of supported ionic catalysts appears in WO 94/03056. When using a Lewis acid ionizing catalyst activator a particularly effective method is that described in WO 96/04319. The support  
15 method of this co-pending application describes the use of a Lewis acid noncoordinating anion precursor (e.g., tris(perfluorophenyl) boron) which is covalently bound to silica-containing supports through retained hydroxy groups which as an initially formed activator complex donates the hydroxyl hydrogens as protons for protonation of the Group 4 transition metal  
20 compound to catalytically active cations. A bulk, or slurry, process utilizing supported, *biscyclopentadienyl* Group 4 metallocenes activated with alumoxane co-catalysts is described as suitable for EPM and EPDM in U.S. patents 5,001,205 and 5,229,478, these processes will additionally be suitable with the catalyst systems of this application. Each of the foregoing  
25 documents is incorporated by reference for purposes of U.S. patent practice. In these examples ENB represents 5-ethylidene-2-norbornene, IPA is isopropyl alcohol, GPC is gel permeation chromatography, TIBAL is triisobutyl aluminum.

30            Though the Examples and the discussion are directed to a single reactor configuration and narrow polydispersity polymers, it is well-known that the use in series of two such reactors each operated so as to achieve different polymer molecular weight characteristics, or by blending polymers from different reactor conditions or utilizing two or more different transition  
35 metal catalysts in one or more reactors, can yield improved processing polymers. The disclosures of U.S. patent 4,722,971 and WO 93/21270 are instructive and are incorporated for purposes of U.S. patent practice. Though



directed to the use of vanadium catalysts, the substitution of the catalyst systems of this invention into one such reactor, or two different invention catalysts into two such reactors, or similar use in two separate polymerizations with subsequent physical blending of the polymer products, will permit tailoring of characteristics (e.g., molecular weights and diene contents) suitable for balancing vulcanization properties with processability. Similarly, the use of mixed catalyst systems, the invention catalysts with themselves or with others, in one or more such reactors will permit preparation of bimodal or multimodal EPC polymers having improved processing properties.

The following examples are presented to illustrate the foregoing discussion. All parts, proportions and percentages are by weight unless otherwise indicated. Although the examples may be directed to certain embodiments of the present invention, they are not to be viewed as limiting the invention in any specific respect. Methods of determining  $M_n$  and monomer contents by NMR and GPC for the illustrative EPDM examples of the invention are described in U.S. patent 5,229,478 which is incorporated by reference for purposes of U.S. patent practice. For measurement of comonomer contents in the EPC elastomers, the method of ASTM D3900 for ethylene-propylene copolymers between 35 and 85 wt.% ethylene was used. Outside that range the NMR method was used. See also, U.S. patent 4,786,697 which is incorporated by reference for purposes of U.S. patent practice.

## EXAMPLES

### Example 1:            Synthesis of EPDM

The polymerizations were conducted in a 500 cc autoclave reactor operated at the temperature of 115 °C in the batch mode for the polymer and semi-batch for the ethylene monomer. The following procedure was used for the polymerizations:

- The reactor was charged with 250 cc of purified hexane, 5 cc of 10 wt.% toluene solution of MAO (activator) and 3 cc of purified ENB (fractional distillation with  $\text{CaH}_2$ ).
- 5 • The reactor was heated to 115 °C, resulting in a hexane vapor pressure of approximately 37 psig (2.5 bar).
- Propylene was added to the reactor to reach 110 psig (7.48 bar) pressure (liquid phase molar conc. = 0.856M).
- 10 • Ethylene was added to the reactor to reach 235 psig (16 bar) pressure (liquid phase conc. = 0.871M ). These conditions determined the initial ethylene/propylene molar ratio equal to 1.018. The ethylene/ENB molar ratio was 10.43.
- 15 • The catalyst solution was pumped to the reactor to maintain the polymerization rate constant as indicated by the make-up flow rate of ethylene to the reactor. The pumping was adjusted to keep this rate at about 0.1 SLPM (standard L/min, standard conditions 1 bar, 21.1 °C),
- 20 to target approximately 10g yield of polymer.
- Irganox® 1076 was added to the hexane solution to the final concentration of 0.1 mg/cc to prevent sample degradation. The polymers were worked-up from the solution by precipitation with IPA.
- 25 After filtering and removing free solvents, the polymer samples were dried under vacuum at 90 °C for about 1 hour.

The analysis of the polymers were done by  $^1\text{H}$ -NMR for ENB content and GPC for EPDM molecular weight.

**Table 1: Results for Example 1**

Catalyst: pentamethylcyclopentadienylbis-  
trimethylsilylamidotitanium dichloride  
 Activator: methylalumoxane  
 Temperature : 115 °C  
 Pressure: 235 psig

Polymer Yield (g)	Catalyst Usage (mg)	Ethylene % wt	Propylene % wt	ENB % wt	M <sub>n</sub>	PD (MWD)
11.7	19.2	73.5	21.22	5.28	100589	2.1
9	19.2	71.6	21.86	6.5	118358	1.85

5    Example 2:            Synthesis of EPDM

The same procedure as described in Example 1 was carried out with the noncoordinating anion activator and with the following differences:

- 10    •     At room temperature, after the reactor was charged with 200 cc of hexane, 50 cc of the  $1.5 \times 10^{-3}$  M of the activator solution in toluene was added. The reactor was then heated up to 115 °C, as in Example 1.
- 15    •     To the pressurized reactor after the addition of ethylene, 10 microliters of 2M TIBAL solution in pentane was added as the scavenger at least one minute before the start of the catalyst pumping.

**Table 2: Results for Example 2**

Catalyst: pentamethylcyclopentadienylbis-trimethylsilylamidotitanium  
dimethyl  
Activator: dimethylanilinium tetra (perfluorophenyl)  
borate  
Temperature: 115 °C  
Pressure: 235 psig

Polymer Yield (g)	Catalyst Usage (mg)	Ethylene % wt	Propylene % wt	ENB % wt	M <sub>n</sub>	PD (MWD)
6.4	3	62.89	31.71	5.4	86303	2.13
11.8	2.4	64.33	30.83	4.84	77145	2.27
4.16	5.64	63.43	31.20	5.37	104497	2.05

5 Comparative Example 2: Synthesis of EPDM

The same procedure as described in Example 2 was carried out the following catalyst:

**Table 3: Results for Comparative Example 2**

Catalyst: cyclopentadienylbis-trimethylsilylamidotitanium dimethyl  
Activator: dimethylanilinium tetra(perfluorophenyl) borate  
Temperature : 115 °C  
Pressure: 235 psig

Polymer Yield (g)	Catalyst Usage (mg)	Ethylene % wt	Propylene % wt	ENB % wt	M <sub>n</sub>	PD
1.3	15	61.64	25.01	13.35	9367	2.58
1.77	30	70.79	20.58	8.63	7293	2.84
2.51	45	68.53	22.48	8.99	8177	3.99

- 5 Comparative Example 2 illustrates the requirement of bulky Cp ligands to the titanium catalyst for improvement of molecular weights. The M<sub>n</sub> for the pentamethylcyclopentadienyl substituted catalyst was at least 10 times higher than for the cyclopentadienyl substituted catalyst of JA 94-80683.

## CLAIMS:

1. A process for the preparation of high molecular weight ethylene- $\alpha$ -olefin-diolefin copolymers comprising contacting in solution at a polymerization temperature at or above about 80 °C, ethylene, one or more  $\alpha$ -olefin monomer, and optionally one or more diene monomer, with a catalyst system prepared from at least one unbridged Group 4 metal compound having a bulky monocyclopentadienyl ligand, a uninegative bulky Group 15 ligand and two uninegative, activation reactive ligands and at least one catalyst activator compound.
2. The process of Claim 1 wherein said unbridged Group 4 metal compound has the formula:



wherein:

M is Zr, Hf or Ti;

20

Cp is a bulky cyclopentadienyl ring which is substituted with from two to five substituent groups R, and each substituent group R is, independently, a radical selected from hydrocarbyl, silyl or germyl radicals having from 1 to 20 carbon, silicon or germanium atoms, substituted hydrocarbyl, silyl or germyl radicals as defined wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, an aryloxy radical or any other radical containing a Lewis acidic or basic functionality; C<sub>1</sub> to C<sub>20</sub> hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; halogen radicals; amido radicals; phosphido radicals; alkoxy radicals; or alkylborido radicals; or, Cp is a cyclopentadienyl ring in which at least two adjacent R-groups are joined together and along with the carbon atoms to which they are attached form a

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C<sub>4</sub> to C<sub>20</sub> ring system which may be saturated, partially unsaturated or aromatic, and substituted or unsubstituted the substitution being of one or more R group as defined above;

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J is the substituted, bulky Group 15 heteroatom ligand which is substituted with two substituent groups R<sup>1</sup>, and each substituent group R<sup>1</sup> is, independently, a radical selected from hydrocarbyl, silyl or germyl radicals having 1 to 20 carbon, silicon or germanium atoms, substituted hydrocarbyl, silyl or germyl radicals as defined wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or an aryloxy radical; C<sub>3</sub> to C<sub>20</sub> hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; halogen radicals; amido radicals; phosphido radicals; alkoxy radicals; or alkylborido radicals; and,

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each Q is independently a radical selected from halide; hydride; substituted or unsubstituted C<sub>1</sub> to C<sub>20</sub> hydrocarbyl; alkoxide; aryloxy; amide; halide or phosphide; or both Q together may be an alkylidene or a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand, with the proviso that where any Q is a hydrocarbyl radical, such Q is not a substituted or unsubstituted cyclopentadienyl radical.

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3. The process according to Claim 2 wherein the R<sup>1</sup> groups are the same and are characterized by having electron-withdrawing characteristics equivalent to or greater than -SiMe<sub>3</sub>.
4. The process according to Claim 1 wherein said polymerization temperature is 100 to 150 °C.
5. The process according to Claim 1 wherein said catalyst activator is an alumoxane compound.

6. The process according to Claim 1 wherein said catalyst activator is an alkylaluminum compound.
- 5 7. The process according to Claim 1 wherein said catalyst activator is an ionizing anion pre-cursor.
8. The process of Claim 1 wherein ethylene, one or more  $\alpha$ -olefin monomer, and one or more diene monomer are contacted with said catalyst system.  
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9. The process of Claim 1 wherein the catalyst is pentamethylcyclopentadienylbis-trimethylsilylamidotitanium dichloride and the activator is methyalumoxane.  
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10. The process of Claim 1 wherein the catalyst is pentamethylcyclopentadienylbis-trimethylsilylamidotitanium dimethyl and the activator is dimethylanilinium tetra (perfluorophenyl) borate.



## AMENDED CLAIMS

[received by the International Bureau on 14 April 1997 (14.04.97);  
original claim 2 amended; new claims 11 and 12 added;  
remaining claims unchanged ( 3 pages)]

1. A process for the preparation of high molecular weight ethylene- $\alpha$ -olefin-diolefin copolymers comprising contacting in solution at a polymerization temperature at or above about 80 °C, ethylene, one or more  $\alpha$ -olefin monomer, and optionally one or more diene monomer, with a catalyst system prepared from at least one unbridged Group 4 metal compound having a bulky monocyclopentadienyl ligand, a uninegative bulky Group 15 ligand and two uninegative, activation reactive ligands and at least one catalyst activator compound.
2. The process of Claim 1 wherein said unbridged Group 4 metal compound has the formula:



wherein:

M is Zr, Hf or Ti;

Cp is a bulky cyclopentadienyl ring which is substituted with from two to five substituent groups R, and each substituent group R is, independently, a radical selected from hydrocarbyl, silyl or germyl radicals having from 1 to 20 carbon, silicon or germanium atoms, substituted hydrocarbyl, silyl or germyl radicals as defined wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, an aryloxy radical or any other radical containing a Lewis acidic or basic functionality; C<sub>1</sub> to C<sub>20</sub> hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; halogen radicals; amido radicals; phosphido radicals; alkoxy radicals; or alkylborido radicals; or, Cp is a cyclopentadienyl ring in which at least two adjacent R-groups are joined together and along with the carbon atoms to which they are attached form a C<sub>4</sub> to C<sub>20</sub> ring system which may be saturated, partially unsaturated or aromatic, and substituted

or unsubstituted the substitution being of one or more R group as defined above;

J is the substituted, bulky Group 15 heteroatom ligand which is substituted with two substituent groups  $R^1$ , and each substituent group  $R^1$  is, independently, a radical selected from hydrocarbyl, silyl or germyl radicals having 4 to 20 carbon, silicon or germanium atoms, substituted hydrocarbyl, silyl or germyl radicals as defined wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or an aryloxy radical;  $C_3$  to  $C_{20}$  hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; halogen radicals; amido radicals; phosphido radicals; alkoxy radicals; or alkylborido radicals; and,

each Q is independently a radical selected from halide; hydride; substituted or unsubstituted  $C_1$  to  $C_{20}$  hydrocarbyl; alkoxide; aryloxy; amide; or phosphide; or both Q together may be an alkylidene or a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand, with the proviso that where any Q is a hydrocarbyl radical, such Q is not a substituted or unsubstituted cyclopentadienyl radical.

3. The process according to Claim 2 wherein the  $R^1$  groups are the same and are characterized by having electron-withdrawing characteristics equivalent to or greater than  $-\text{SiMe}_3$ .
4. The process according to Claim 1 wherein said polymerization temperature is 100 to 150 °C.
5. The process according to Claim 1 wherein said catalyst activator is an alumoxane compound.
6. The process according to Claim 1 wherein said catalyst activator is an alkylaluminum compound.

7. The process according to Claim 1 wherein said catalyst activator is an ionizing anion pre-cursor.
8. The process of Claim 1 wherein ethylene, one or more  $\alpha$ -olefin monomer, and one or more diene monomer are contacted with said catalyst system.
9. The process of Claim 1 wherein the catalyst is pentamethylcyclopentadienylbis-trimethylsilylamidotitanium dichloride and the activator is methyalumoxane.
10. The process of Claim 1 wherein the catalyst is pentamethylcyclopentadienylbis-trimethylsilylamidotitanium dimethyl and the activator is dimethylanilinium tetra (perfluorophenyl) borate.
11. The process according to Claims 1, 2, 9 or 10 wherein said high molecular weight ethylene- $\alpha$ -olefin-diolefin copolymers have an  $M_n$  greater than than 55,000 and at least 10 mol.%  $\alpha$ -olefin incorporation.
12. The process according to Claim 11 wherein said ethylene- $\alpha$ -olefin-diolefin copolymers comprises from 0.5 to 20 wt.% diene monomer.

## STATEMENT UNDER ARTICLE 19

The invention of this application is addressed in major part to the problem of preparation of high molecular weight polyethylene copolymers utilizing monocyclopentadienyl metallocene catalysts in solution polymerization processes. New claims 10 and 11 incorporate these product elements and amended claim 2 further clarifies the bulky J substituent by disclaimer of subject matter in the prior art. Specifically, new claim 10 defines both minimum molecular weight and minimum  $\alpha$ -olefin content of typical plastomers and elastomers of the invention. Claim 11 defines diene monomer content of preferred embodiment. Support for the amendments appear in the text of the international application as filed at page 6 lines 3-10; page 7, lines 13-14; and in both of Examples 1 and 2. The amendment to claim 2 recites that the J amido substituent must contain 4 or more C, Si or Ge atoms. The ISR identifies both of EP-A- 0 476 671 and JP-A- 06 080 683 as being of particular relevance. However, the identified documents do not address the preparation of high molecular weight polyethylene copolymers.

EP-A- 0 476 671 teaches the use of monocyclopentadiene-containing indenyl metallocene catalysts for ethylene copolymers, the catalysts additionally comprising either two or three ligands described to be  $-NR_1$  where  $R_1$  is a  $C_1 - C_4$  alkyl. The examples illustrate the use of methyl, ethyl and propyl  $R_1$  substituents for ethylene copolymers having both low molecular weights, as apparent from the reported  $I_2$  melt index properties ( $\geq 1.4$ ), and low  $\alpha$ -olefin contents as apparent from the reported densities ( $> 0.92$ ). These catalyst systems do not suggest or teach the necessity of the bulky substituent on the invention Group 15 ligand.

JP-A- 06 080 683 illustrates the use of (cyclopentadienyl)(*bis*trimethylsilylamido) titanium dichloride for the production of atactic polypropylene. Though this catalyst is of limited effectiveness for olefin polymerization, the examples of Applicants' illustrate that under similar conditions, the catalysts of the amended claims are capable of producing substantially higher molecular weight copolymers than those produced with the catalyst exemplified as representative in this document.

# INTERNATIONAL SEARCH REPORT

Internat:      Application No

PCT/US 96/17224

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6    C08F210/18    C08F2/06    C08F4/645

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6    C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 476 671 A (DOW CHEMICAL CO) 25 March 1992 see page 2, line 50 - page 4, line 10 see page 6, line 11 - line 13 see page 6, line 50 - line 53; claims; examples; table 1 ---	1,2,4,5
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X		1-3
	-/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

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- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Internat Application No  
PCT/US 96/17224

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 264 405 A (CANICH JO ANN M) 23 November 1993 cited in the application see claims; examples 40-44 ---	1-7,9,10
A	WO 94 00500 A (EXXON CHEMICAL PATENTS INC) 6 January 1994 see page 30, line 23 - page 31, line 22; claims; examples 1-4 ---	1-8
A	JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 467, 1994, XP002023906 A. MARTIN ET AL.: "Dialkylamido Derivatives of..." cited in the application see page 79 - page 84 -----	1,2

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Internat Application No

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		US-A- 5194532	16-03-93
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JP-A-06080683	22-03-94	NONE	
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